Spin State

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A Unified Treatment of the Relationship Between Ligand Substituents and Spin State in a Family of Iron(II) Complexes

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Abstract: *The influence of ligands on the spin state of a metal ion is of central importance for bioinorganic chemistry, and the production of base-metal catalysts for synthesis applications. Complexes derived from $[Fe(bpp)_2]^{2+}$ (bpp = 2,6-di{pyrazol-1-yl}pyridine) can be high-spin, low-spin, or spin-crossover (SCO) active depending on the ligand substituents. Plots of the SCO midpoint temperature ($T_{1/2}$) in solution vs. the relevant Hammett parameter show that the low-spin state of the complex is stabilized by electron-withdrawing pyridyl ("X") substituents, but also by electron-donating pyrazolyl ("Y") substituents. Moreover, when a subset of complexes with halogeno X or Y substituents is considered, the two sets of compounds instead show identical trends of a small reduction in $T_{1/2}$ for increasing substituent electronegativity. DFT calculations reproduce these disparate trends, which arise from competing influences of pyridyl and pyrazolyl ligand substituents on Fe-L σ and π bonding.*

The ability of first-row transition ions to adopt different spin states in strong or weak ligand fields is of great importance to their catalysis and reactivity.[1–3] For example, fundamental mechanistic steps in biological and synthetic oxidation catalysis involve a change in spin state at an iron catalyst center, described as two-state reactivity.[3] Catalysts with different resting spin states follow different pathways through these two-state processes, leading to altered reactivity and product distributions.[4] Similar considerations also apply for "base-metal" catalysts for organometallic reactions,[5] which give access to high-spin active species with different reactivity patterns compared to conventional precious-metal catalysts.[6,7] Another consequence of spin-state dichotomy is the phenomenon of spin crossover (SCO), where a molecular or framework compound exhibits a transition between high- and low-spin states under a physical stimulus.[8,9] SCO compounds have been developed into versatile molecular switches for molecular materials chemistry and nanoscience.[9,10]

The relationship between chemical structure and spin state is central to these phenomena.[2,11] A sterically crowded ligand sphere generally leads to high-spin complexes.[12] However, the effect of ligand electronic character on metal-ion spin state is less clear-cut, with electron-withdrawing substituents being reported to stabilize either the low-spin[13–16] or the high-spin state[17,18] in different series of compounds. While the literature includes data from solution and the solid-state, these effects are best quantified by solution measurements which determine a complex's spin state in the absence of crystal-packing effects or any other influences from a rigid solid lattice.[19] We report herein a comprehensive study to resolve this contradiction, through a survey of twenty-five complexes from the $[Fe(bpp^{X,Y})_2]^{2+}$ family ($bpp^{X,Y}$ = a 2,6-di(pyrazol-1-yl)pyridine derivative; Scheme 1).[20] Our results show that substituents at the X and Y sites have different, opposing effects on the iron-atom spin state.

The spin states of these complexes were measured in solution by the variable-temperature Evans method,[21] in $(CD_3)_2CO$ or CD_3NO_2 depending on their solubility (Figure 1). Our use of different weakly interacting solvents should cause only small perturbations to the data.[22] The complexes with $X = NH_2$ and NMe_2 remain high-spin within experimental error over the liquid range of the solvent. All the other complexes exhibit SCO, although the midpoint temperature of the transition ($T_{1/2}$) varies from 158 K (X = OMe) ≤ $T_{1/2}$ ≤ 305 K (X = NO_2).[23] Where they could be derived, thermodynamic parameters for these equilibria are mostly similar to other $[Fe(bpp^{X,Y})_2]^{2+}$ complexes.[20,23] However, higher ΔH and ΔS values for $[Fe(bpp^{CO_2H,H})_2]^{2+}$ and $[Fe(bpp^{SO_2Me,H})_2]^{2+}$ imply that ligand-dissociation equilibria in those complexes may be occurring, promoted by the nucle-

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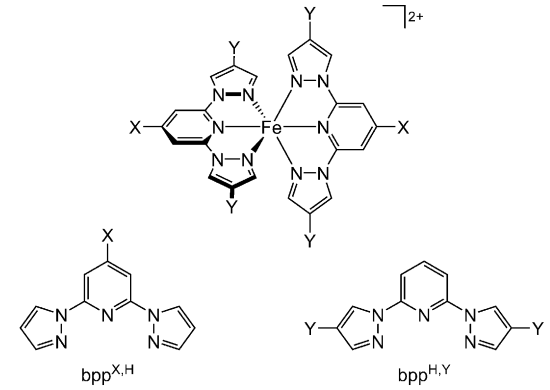

X = H
Me, CH_2SCN, CO_2H,
F, Cl, Br, I
NH_2, NMe_2, NO_2
OH, OMe
SH, SSbpp, SMe, SOMe,
SO_2Me

Y = H
Me, CH_2OH, *t*Bu, CO_2Et
Cl, Br, I

Scheme 1. Different substitution patterns of $[Fe(bpp)_2]^{2+}$ (top), and the different $bpp^{X,Y}$ ligands referred to in this study (bottom).

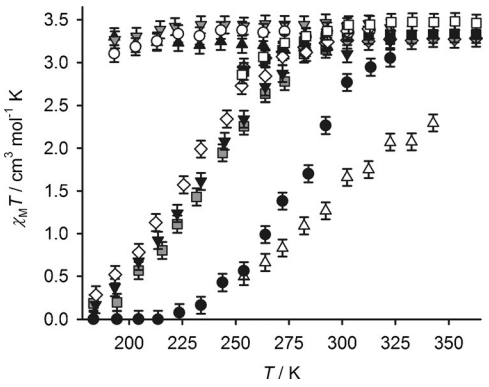

Figure 1. Solution-phase magnetic susceptibilty data: $[Fe(bpp^{OH,H})_2][BF_4]_2$ (○); $[Fe(bpp^{OMe,H})_2][PF_6]_2$ (▼); $[Fe(bpp^{NH_2,H})_2][BF_4]_2$ (▲); $[Fe(bpp^{Me,H})_2][BF_4]_2$ (□); $[Fe(bpp^{F,H})_2][BF_4]_2$ (◆); $[Fe(bpp^{pz,H})_2][BF_4]_2$ (■); $[Fe(bpp^{Cl,H})_2][BF_4]_2$ (◇); $[Fe(bpp^{Br,H_2})][BF_4]_2$ (▼); $[Fe(bpp^{I,H})_2][BF_4]_2$ (■); $[Fe(bpp^{CO_2H,H})_2][BF_4]_2$ (●); $[Fe(bpp^{NO_2,H})_2][BF_4]_2$ (△).[23]

ophilic carboxylic and sulfoxide substituents. Since ligand dissociation only occurs in the labile high-spin state of a complex, as a pre-equilibrium to SCO, it will have little effect on $T_{1/2}$.[19,22]

Plots of $T_{1/2}$ versus the substituent electronegativity (χ^P [24]) for $[Fe(bpp^{X,H})_2]^{2+}$ and $[Fe(bpp^{H,Y})_2]^{2+}$ show identical correlations for substituents with weak π-bonding character (X, Y = halogen and SH; Figure 2). Within this series, electronegative substituents lower $T_{1/2}$ to a small extent, so less electron-rich X and Y groups slightly stabilize the high-spin state. That is consistent with basic ligand-field arguments. However, simple X and Y substituents with π-bonding resonance properties (X, Y = CH_3, NH_2, and OH) deviate strongly from this relationship. That implies metal–ligand π bonding must contribute to the spin states of these complexes.

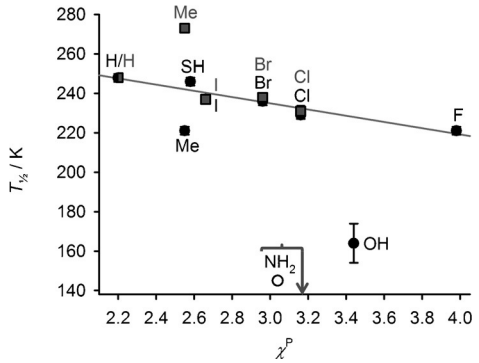

Figure 2. Plot of $T_{1/2}$ versus the substituent electronegativity (χ^P) for $[Fe(bpp^{X,H})_2]^{2+}$ (●) and $[Fe(bpp^{H,Y})_2]^{2+}$ (■) complexes with simple heteroatom X and Y substituents.[23] $T_{1/2}$ for X = NH_2 (○) represents an upper limit for that measurement, since the complex is fully high-spin over the liquid range of the solvent. The line shows the best fit correlation ($R^2 = 0.91$), omitting the X/Y = Me, OH and NH_2 datapoints.

Resonance effects for ligand "X" substituents are accounted for by the σ_p Hammett parameter.[25] A plot of $T_{1/2}$ versus σ_p for $[Fe(bpp^{X,H})_2]^{2+}$ contains some scatter, particularly around $\sigma_p \approx 0$, but shows a positive linear correlation (Figure 3, top). That is, more electron-withdrawing pyridyl X substituents stabilize the low-spin state of $[Fe(bpp^{X,H})_2]^{2+}$. This result is consistent with previous studies of complexes with pyridyl donor ligands,[14–16] but it is the

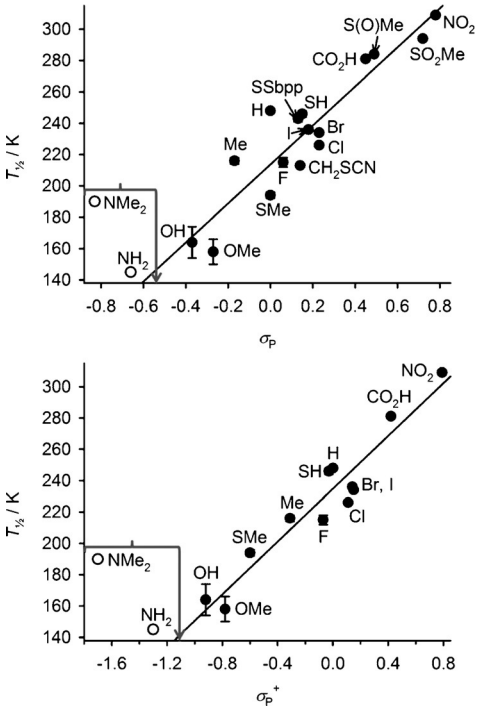

Figure 3. Plots of $T_{1/2}$ for $[Fe(bpp^{X,H})_2]^{2+}$ versus the X substituent Hammett parameters σ_p (top) and σ_p^+ (bottom; Table S1 in the Supporting Information).[23] Error bars are mostly smaller than the symbols on the graph. The lines show the best fit correlation ($R^2 = 0.86$ [top] and 0.92 [bottom]), omitting the X = NH_2 and NMe_2 datapoints (○) which represent the upper limits for those $T_{1/2}$ measurements.

opposite trend to the electronegativity plot (Figure 2). An improved correlation is found when $T_{1/2}$ is plotted against σ_p^+, a modified Hammett parameter accounting for conjugation of the ligand substitutents with a positively charged reaction center (Figure 3, bottom).[25] Hence, these data appear to be influenced by π bonding between the Lewis acidic Fe^{2+} ion and the ligand pyridyl donors. In contrast, a plot of $T_{1/2}$ for $[Fe(bpp^{H,Y})_2]^{2+}$ versus the relevant substituent Hammett parameter (σ_M[25]) shows the opposite trend from the $[Fe(bpp^{X,H})_2]^{2+}$ series. That is, more electron-withdrawing pyrazolyl substituents stabilize the high-spin state in $[Fe(bpp^{H,Y})_2]^{2+}$ derivatives, even when substituent resonance effects are included (Figure 4). Such a dependence of $T_{1/2}$ on the positioning of ligand substituents, in the absence of any steric influence, has not been noted before.

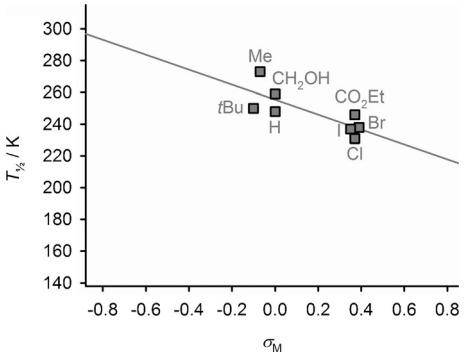

Figure 4. Plot of $T_{1/2}$ versus the Y substituent Hammett parameters σ_M for $[Fe(bpp^{H,Y})_2]^{2+}$ complexes with different Y substituents.[23] Error bars are shown, but are smaller than the symbols on the graph. The line shows the best fit correlation ($R^2 = 0.61$). The graph is drawn for the same range as Figure 3 (top), to aid comparison.

This question was probed by density functional (DFT) calculations of $[Fe(bpp^{X,Y})_2]^{2+}$ using the BP86 functional. The correlation between the measured $T_{1/2}$ and the computed difference between the high-spin and low-spin total energies, ΔE_{rel}(HS-LS), is very good despite the relatively simplistic computational method used,[26] with a R^2 correlation coefficient of 0.79.[23] The agreement between ΔE_{rel}(HS-LS) and the X or Y substituent Hammett parameter is moderate when all the compounds are plotted together, but improves when $[Fe(bpp^{X,H})_2]^{2+}$ and $[Fe(bpp^{H,Y})_2]^{2+}$ are considered separately (Figure 5). Hence, the calculations have captured the spin-state behavior of the two sets of compounds.

The σ and π contributions to Fe–L bonding for each $bpp^{X,Y}$ ligand were quantified by considering the d-orbital energies of the low-spin compounds. Electron-withdrawing X or Y substituents lower the energy of all the metal d-orbitals (Figure 6), but the effect is 2–3 times greater for Y substituents than for X substituents since there as twice as many Y substituents as X groups in a $[Fe(bpp^{X,Y})_2]^{2+}$ molecule. The X substituents in $[Fe(bpp^{X,H})_2]^{2+}$ have a greater effect on the averaged t_{2g} orbital energies than on the e_g orbitals, from the slopes of their least squares correlations (Figure 6). In contrast, Y substituents in $[Fe(bpp^{H,Y})_2]^{2+}$ have a much larger influence on the averaged e_g orbital energies than on the t_{2g} energies (Figure 6).[27]

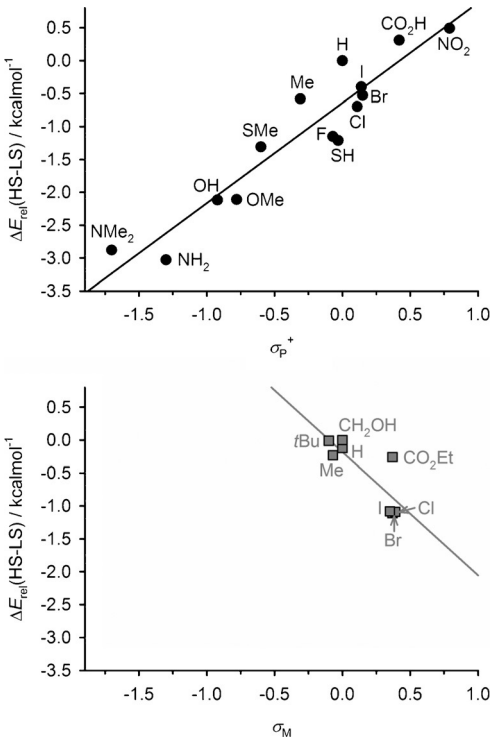

Figure 5. Plot of the relevant substituent Hammett parameter vs. the computed energy difference between the high- and low-spin states relative to X = Y = H [ΔE_{rel}(HS-LS)], for: $[Fe(bpp^{X,H})_2]^{2+}$ (top, ●) and $[Fe(bpp^{H,Y})_2]^{2+}$ (bottom, ■).[23] The graphs are plotted to the same scale to aid comparison, and the lines show the best fit correlations ($R^2 = 0.89$ [top] and 0.67 [bottom][28]).

The relationship between $T_{1/2}$ and the $bpp^{X,Y}$ ligand is a competition between Fe–L σ- and π-bonding effects. Electron-withdrawing substituents inductively lower the energy of the bpp lone pairs, weakening the σ ligand field and thus stabilizing the high-spin state. Conversely, electron-withdrawing substituents also reduce the energy of the $bpp^{X,Y}$ π* MOs, which increases the ligand field by strengthening Fe→bpp π backbonding and favors the low-spin state. Fe–L π-bonding effects dominate in the $[Fe(bpp^{X,H})_2]^{2+}$ series, where electron-withdrawing substituents stabilize the t_{2g} orbital manifold more strongly than the e_g, thus increasing the ligand field and raising $T_{1/2}$. In contrast, the spin state of the $[Fe(bpp^{H,Y})_2]^{2+}$ family is controlled by Fe–L σ bonding, since electron-withdrawing Y substituents stabilize the e_g orbitals more strongly, promoting the high-spin state and lowering $T_{1/2}$.

When complexes with halogen X and Y substituents are considered separately, the stabilization of $E_{av}(e_g)$ by electron-withdrawing substituents is approximately 25% greater than $E_{av}(t_{2g})$ for both sets of complexes.[23] Thus, electronegative halogen X and Y groups both reduce $T_{1/2}$, and the essentially identical $T_{1/2}$ values shown by $[Fe(bpp^{X,H})_2]^{2+}$ and $[Fe(bpp^{H,Y})_2]^{2+}$ when X, Y = a halogen (Figure 2) are also supported by this computational study, despite being contrary to the rest of the data.[17]

These results reconcile the differing conclusions from earlier studies. Electron-withdrawing substitutents indeed

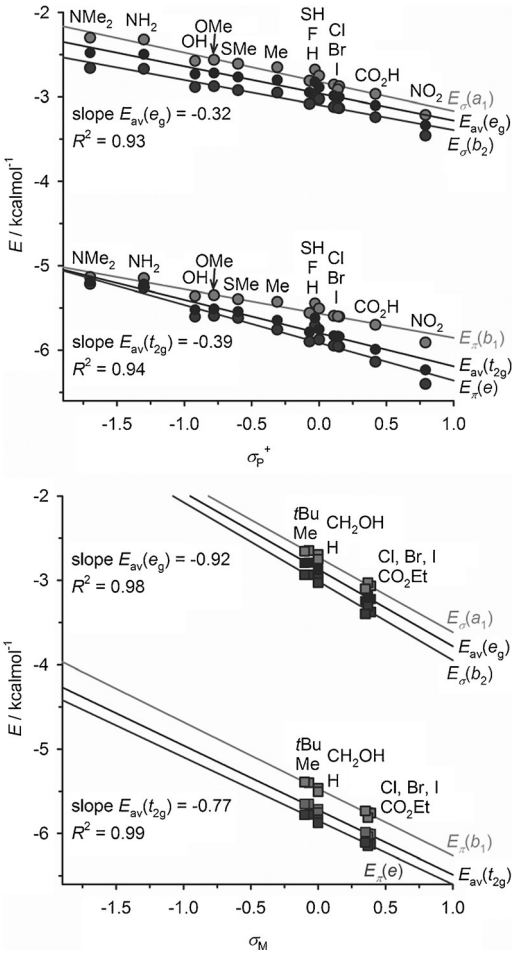

Figure 6. Plot of the relevant substituent Hammett parameter versus the computed d-orbital energies for $[Fe(bpp^{X,H})_2]^{2+}$ (top, circles) and $[Fe(bpp^{H,Y})_2]^{2+}$ (bottom, squares).[23,27] The average orbital energies of the t_{2g} and e_g subshells are also shown, along with their best fit correlations and slopes.

stabilize either the low-spin[13–16] or the high-spin state[17,18] of a complex, depending on their position in the molecule and on which types of substituent are considered. The relationship between ligand design and metal-ion spin state is a fine balance between opposing M–L σ- and π-bonding effects. Rational design of a complex with defined spin-state properties for SCO, catalysis, or other applications requires consideration of all these aspects of the metal–ligand interaction.

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[23] The Supporting Information contains synthetic, crystallographic, and computational procedures, and full characterization data for

the seven new $[Fe(bpp^{X,Y})_2]^{2+}$ complexes; crystallographic Figures and Tables; solution and solid phase magnetic susceptibility data; and Tables and graphs of computed molecular geometries, and spin state and orbital energies.
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[27] In the idealized D_{2d} symmetry of the $[Fe(bpp^{X,Y})_2]^{2+}$ molecule, the metal d-orbitals transform as: *e* (d_{xz} and d_{yz}); b_1 ($d_{x^2-y^2}$, which has M–L π symmetry in the axis frame used); b_2 (d_{xy}, a M–L σ symmetry orbital in this axis frame); and, a_1 (d_{z^2}). O_h symmetry labels are used when the σ- and π-symmetry metal d orbitals are discussed collectively.
[28] The weaker agreement between ΔE_{rel}(HS-LS) and σ_M for the $[Fe(bpp^{H,Y})_2]^{2+}$ series reflects an outlier data point for Y = CO_2Et (Figure 5). Anomalous spin-state energies were also calculated for a carboxy-substituted member of a family of iron(II) complexes of pyridyl-containing macrocyclic ligands.[15b]

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